

Polymer Electrolyte with Aromatic Sulfone Crosslinking

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Field of the Invention

This invention relates to a method of obtaining crosslinked polymers having pendent sulfonic acid groups by crosslinking through the sulfonic acid groups or their precursors with aromatic crosslinkers or aromatic pendent crosslinking groups to form aromatic sulfones. Such crosslinked polymers may be used to make polymer electrolyte membranes (PEM's) that may be used in electrolytic cells such as fuel cells.

Background of the Invention

Copolymers of tetrafluoroethylene (TFE) and a co-monomer according to the formula: $\text{FSO}_2\text{-CF}_2\text{-CF}_2\text{-O-CF(CF}_3\text{)-CF}_2\text{-O-CF=CF}_2$ are known and sold in sulfonic acid form, i.e., with the $\text{FSO}_2\text{-}$ end group hydrolyzed to $\text{HSO}_3\text{-}$, under the trade name Nafion® by DuPont Chemical Company, Wilmington, Delaware. Nafion® is commonly used in making polymer electrolyte membranes for use in fuel cells.

Copolymers of tetrafluoroethylene (TFE) and a co-monomer according to the formula: $\text{FSO}_2\text{-CF}_2\text{-CF}_2\text{-O-CF=CF}_2$ are known and used in sulfonic acid form, i.e., with the $\text{FSO}_2\text{-}$ end group hydrolyzed to $\text{HSO}_3\text{-}$, in making polymer electrolyte membranes for use in fuel cells.

U.S. Pat. App No. 10/325,278, filed December 19, 2002, the disclosure of which is incorporated herein by reference, discloses a polymer electrolyte membrane having a thickness of 90 microns or less and comprising a polymer, said polymer comprising a highly fluorinated backbone and recurring pendant groups according to the formula:



where Y is H⁺ or a monovalent cation such as an alkali metal cation. Typically, the membrane is a cast membrane. Typically, the polymer has a hydration product of greater than 22,000. Typically, the polymer has an equivalent weight of 800-1200.

International Patent Application Publication No. WO 01/27167 purportedly
5 discloses a crosslinked fluorocarbon polymeric composition having hydrophilic functional groups which is crosslinked with fluorinated crosslinking groups.

U.S. Patent Application Publication No. 2003/0032739 discloses a covalently crosslinked polymer or polymer membrane consisting of one or more polymers, which may bear precursors of cation exchange groups, which are crosslinked through the
10 reaction of sulfinate groups -SO₂Me on the polymer with crosslinkers which may include halo aromatics to form cross-linking bridges which may include: polymer-SO₂-arylene-SO₂-polymer.

U.S. Patent No. 6,090,895 discloses a method for making crosslinked acidic polymers useful as ion conductive membranes, such as crosslinked sulfonated polyether
15 ketones, sulfonated polysulfones, sulfonated polystyrenes, and other acidic polymers, by crosslinking with a species which generates an acidic functionality. The crosslinker preferably binds to acid functions by conversion of acid groups to imide functionality, which, due to the acidity of the N-H bonds therein, compensate for the acidity lost by the occupation of the acid groups and thus preserve membrane conductivity while
20 contributing to membrane strength and resistance to swelling.

U.S. Patent Application Publication No. 2003/0092940 discloses a method for making aromatic-imide and aromatic-methylidynetrisulfonyl species by reaction of aromatic species with a reactant according to the formula:



25 wherein Q is C or N; wherein each X is independently selected from the group consisting of halogens, typically F or Cl; wherein each R₁ is independently selected from the group consisting of aliphatic and aromatic groups, which may or may not be straight-chain, branched, cyclic, heteroatomic, polymeric, halogenated, fluorinated or substituted; wherein m is greater than 0; wherein m + n = 2 when Q is N; and wherein
30 m + n = 3 when Q is C. Ar may be derived from an aromatic polymeric compound. In addition, the reference discloses compounds according to the formula:

(Ar-SO₂-)_m-QH-(-SO₂-R₁)_n wherein R₁ comprises a highly acidic group selected from sulfonic acid, carboxylic acid and phosphonic acid, and Ar is derived from an aromatic compound.

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Summary of the Invention

The present invention provides crosslinked polymers and method of making crosslinked polymers by a comprising the steps of: a) providing a highly fluorinated polymer comprising pendent groups which include a group according to the formula -SO₂X, wherein each X is independently selected from F, Cl, Br, I, -OH or -O-SO₂R²

10 wherein R² is an aliphatic group containing 1-18 carbon atoms which may be substituted; and b) reacting the polymer with a crosslinking agent according to the formula Ar_nR¹, wherein each Ar is selected independently from aromatic groups containing 6-24 carbon or nitrogen atoms and wherein each Ar may be substituted, wherein R¹ is a direct bond or an aromatic or aliphatic linking group, wherein R¹ may
15 be straight-chain, branched, cyclic, heteroatomic, polymeric, halogenated, fluorinated or substituted, and where n is at least 2, to form crosslinks comprising units according to the formula (-SO₂Ar)_nR¹. In one embodiment, the polymer comprises pendent groups that include -SO₂F and at least a portion of the -SO₂F groups are then converted to -SO₂Cl or -SO₂-O-SO₂R² for reaction. In one embodiment, the polymer is formed into
20 a membrane prior to crosslinking, typically one having a thickness of 90 microns or less. Typically, the remaining -SO₂X groups are converted to sulfonic acid groups after crosslinking.

In another aspect, the present invention provides a highly fluorinated crosslinked polymer comprising: a backbone, pendent groups which comprise sulfonic
25 acid groups, and crosslinks comprising units according to the formula (-SO₂Ar)_nR¹ wherein each Ar is selected independently from aromatic groups containing 6-24 carbon or nitrogen atoms and wherein each Ar may be substituted, wherein R¹ is a direct bond or an aromatic or aliphatic linking group, wherein R may be straight-chain, branched, cyclic, heteroatomic, polymeric, halogenated, fluorinated or substituted, and

where n is at least 2. In one embodiment, the polymer is a polymer electrolyte membrane, typically having a thickness of 90 microns or less. Typical pendent groups include groups according to the formula $-O-(CF_2)_4-SO_3H$ and groups according to the formula $-O-CF_2-CF(CF_3)-O-CF_2-CF_2-SO_3H$.

5 In another aspect, the present invention provides a method of making a crosslinked polymer comprising the steps of: a) providing a highly fluorinated polymer comprising first pendent groups which include a group according to the formula $-SO_2X$, wherein each X is independently selected from F, Cl, Br, I, $-OH$ or $-O-SO_2R^2$ wherein R^2 is an aliphatic group containing 1-18 carbon atoms which may be
10 substituted, and second pendent groups which include groups $-Ar$, wherein each Ar is selected independently from aromatic groups containing 6-24 carbon or nitrogen atoms and wherein each Ar may be substituted; and b) reacting the polymer to form crosslinks between the first and second pendent groups comprising units according to the formula $-SO_2Ar-$. In one embodiment, the polymer comprises first pendent groups that include
15 $-SO_2F$ and at least a portion of the $-SO_2F$ groups are then converted to $-SO_2Cl$ or $-SO_2-O-SO_2R^2$ for reaction. In one embodiment, the polymer is formed into a membrane prior to crosslinking, typically one having a thickness of 90 microns or less. Typically, the remaining $-SO_2X$ groups are converted to sulfonic acid groups after crosslinking.

20 In another aspect, the present invention provides a highly fluorinated crosslinked polymer comprising: a backbone, pendent groups which comprise sulfonic acid groups, and crosslinks comprising units according to the formula $-SO_2Ar-$ wherein each Ar is selected independently from aromatic groups containing 6-24 carbon or nitrogen atoms and wherein each Ar may be substituted. In one embodiment, the
25 polymer is a polymer electrolyte membrane, typically having a thickness of 90 microns or less. Typical pendent groups include groups according to the formula $-O-(CF_2)_4-SO_3H$ and groups according to the formula $-O-CF_2-CF(CF_3)-O-CF_2-CF_2-SO_3H$.

In this application:

“equivalent weight” (EW) of a polymer means the weight of polymer which will neutralize one equivalent of base;

5 “hydration product” (HP) of a polymer means the number of equivalents (moles) of water absorbed by a membrane per equivalent of sulfonic acid groups present in the membrane multiplied by the equivalent weight of the polymer; and

“highly fluorinated” means containing fluorine in an amount of 40 wt% or more, typically 50 wt% or more and more typically 60 wt% or more.; and

10 “substituted” means, for a chemical species, substituted by conventional substituents which do not interfere with the desired product or process, e.g., substituents can be alkyl, alkoxy, aryl, phenyl, halo (F, Cl, Br, I), cyano, nitro, etc.

Detailed Description

Briefly, the present invention provides a method of obtaining crosslinked
15 polymers having pendent sulfonic acid groups by crosslinking through the sulfonic acid groups or their precursors with aromatic crosslinkers or aromatic pendent crosslinking groups to form aromatic sulfones. Such crosslinked polymers may be used to make polymer electrolyte membranes (PEM’s) that may be used in electrolytic cells such as fuel cells.

20 PEM’s manufactured from the crosslinked polymer according to the present invention may be used in the fabrication of membrane electrode assemblies (MEA’s) for use in fuel cells. An MEA is the central element of a proton exchange membrane fuel cell, such as a hydrogen fuel cell. Fuel cells are electrochemical cells which produce usable electricity by the catalyzed combination of a fuel such as hydrogen and
25 an oxidant such as oxygen. Typical MEA’s comprise a polymer electrolyte membrane (PEM) (also known as an ion conductive membrane (ICM)), which functions as a solid electrolyte. One face of the PEM is in contact with an anode electrode layer and the opposite face is in contact with a cathode electrode layer. Each electrode layer includes electrochemical catalysts, typically including platinum metal. Gas diffusion layers
30 (GDL’s) facilitate gas transport to and from the anode and cathode electrode materials and conduct electrical current. The GDL may also be called a fluid transport layer

(FTL) or a diffuser/current collector (DCC). The anode and cathode electrode layers may be applied to GDL's in the form of a catalyst ink, and the resulting coated GDL's sandwiched with a PEM to form a five-layer MEA. Alternately, the anode and cathode electrode layers may be applied to opposite sides of the PEM in the form of a catalyst ink, and the resulting catalyst-coated membrane (CCM) sandwiched with two GDL's to form a five-layer MEA. The five layers of a five-layer MEA are, in order: anode GDL, anode electrode layer, PEM, cathode electrode layer, and cathode GDL. In a typical PEM fuel cell, protons are formed at the anode via hydrogen oxidation and transported across the PEM to the cathode to react with oxygen, causing electrical current to flow in an external circuit connecting the electrodes. The PEM forms a durable, non-porous, electrically non-conductive mechanical barrier between the reactant gases, yet it also passes H^+ ions readily.

The polymer to be crosslinked comprises a backbone, which may be branched or unbranched but is typically unbranched. The backbone is fluorinated, typically highly fluorinated, and more typically perfluorinated. The backbone may comprise units derived from tetrafluoroethylene (TFE), i.e., typically $-CF_2-CF_2-$ units, and units derived from co-monomers, typically including at least one according to the formula $CF_2=CY-R^{10}$ where Y is typically F but may also be CF_3 , and where R^{10} is a first pendant group which includes a group according to the formula $-SO_2X$ wherein X is selected from F, Cl, Br, I, $-OH$ or $-O-SO_2R^2$ wherein R^2 is an aliphatic group containing 1-18 carbon atoms which may be substituted. Where $-SO_2X$ is a sulfonyl halide, X is most typically F. In an alternative embodiment, first pendant groups R^{10} may be added to the backbone by grafting. Typically, first pendant groups R^{10} are highly fluorinated and more typically perfluorinated. R^{10} may be aromatic or non-aromatic. Typically, R^{10} is $-R^{11}-SO_2X$, where R^{11} is a branched or unbranched perfluoroalkyl or perfluoroether group comprising 1-15 carbon atoms and 0-4 oxygen atoms. R^{11} is typically $-O-R^{12}-$ wherein R^{12} is a branched or unbranched perfluoroalkyl or perfluoroether group comprising 1-15 carbon atoms and 0-4 oxygen

atoms. R^{11} is more typically $-O-R^{13}$ wherein R^{13} is a perfluoroalkyl group comprising 1-15 carbon atoms. Examples of R^{11} include:

$-(CF_2)_n-$ where n is 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 or 15

$-(CF_2CF(CF_3))_n-$ where n is 1, 2, 3, 4, or 5

5 $-(CF(CF_3)CF_2)_n-$ where n is 1, 2, 3, 4, or 5 $-(CF_2CF(CF_3))_n-CF_2-$ where n is 1, 2, 3 or 4

$(-O-CF_2CF_2)_n-$ where n is 1, 2, 3, 4, 5, 6 or 7

$(-O-CF_2CF_2CF_2)_n-$ where n is 1, 2, 3, 4, or 5

$(-O-CF_2CF_2CF_2CF_2)_n-$ where n is 1, 2 or 3

10 $(-O-CF_2CF(CF_3))_n-$ where n is 1, 2, 3, 4, or 5

$(-O-CF_2CF(CF_2CF_3))_n-$ where n is 1, 2 or 3

$(-O-CF(CF_3)CF_2)_n-$ where n is 1, 2, 3, 4 or 5

$(-O-CF(CF_2CF_3)CF_2)_n-$ where n is 1, 2 or 3

$(-O-CF_2CF(CF_3))_n-O-CF_2CF_2-$ where n is 1, 2, 3 or 4

15 $(-O-CF_2CF(CF_2CF_3))_n-O-CF_2CF_2-$ where n is 1, 2 or 3

$(-O-CF(CF_3)CF_2)_n-O-CF_2CF_2-$ where n is 1, 2, 3 or 4

$(-O-CF(CF_2CF_3)CF_2)_n-O-CF_2CF_2-$ where n is 1, 2 or 3

$-O-(CF_2)_n-$ where n is 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13 or 14

R^{10} is typically $-O-CF_2CF_2CF_2CF_2-SO_2X$ or $-O-CF_2-CF(CF_3)-O-CF_2-$

20 CF_2-SO_2X and most typically $-O-CF_2CF_2CF_2CF_2-SO_2X$. The $-SO_2X$ group is most typically $-SO_2F$ during polymerization, i.e., X is F. The $-SO_2X$ group is typically converted to $-SO_3H$ at some point prior to use of the fluoropolymer as an polymer electrolyte. The fluoromonomer providing first side group R^{10} may be synthesized by any suitable means, including methods disclosed in U.S. Pat. No. 6,624,328.

25 The polymer may be made by any suitable method, including emulsion polymerization, extrusion polymerization, polymerization in supercritical carbon dioxide, solution or suspension polymerization, and the like, including methods

disclosed in U.S. Pat. App. No. __/__, filed October 30, 2003 [Atty Docket No. 58585US002] and references cited therein.

Where the $\text{-SO}_2\text{X}$ group is $\text{-SO}_2\text{F}$ during polymerization, some of the $\text{-SO}_2\text{F}$ groups may be converted to more reactive groups prior to crosslinking, such as $\text{-SO}_2\text{Cl}$,
5 $\text{-SO}_2\text{Br}$, $\text{-SO}_2\text{I}$ or $\text{-O-SO}_2\text{R}^2$ wherein R^2 is an aliphatic group containing 1-18 carbon atoms which may be substituted, more typically containing 1-8 carbon atoms, and most typically methyl or ethyl. Typically, between 1 and 50% of $\text{-SO}_2\text{F}$ groups are converted to more reactive groups. $\text{-SO}_2\text{F}$ groups may be converted by any suitable method.

$\text{-SO}_2\text{F}$ groups may be converted to $\text{-SO}_2\text{Cl}$ groups by any suitable method. In one such
10 method, $\text{-SO}_2\text{F}$ groups are reduced to $\text{-SO}_2\text{H}$ by use of a suitable reducing agent, such as a hydrazine or mercaptan such as mercaptoethanol, and subsequently converted to $\text{-SO}_2\text{Cl}$ with a hypochloride. In another such method, $\text{-SO}_2\text{F}$ groups may be converted to $\text{-SO}_2\text{Cl}$ groups by reaction with oxalyl chloride in dry toluene with pyridine catalyst. $\text{-SO}_2\text{F}$ groups may be converted to $\text{-O-SO}_2\text{R}^2$ groups by any suitable method. In one
15 such method, $\text{-SO}_2\text{F}$ groups are converted by exchange with $\text{R}^2\text{-SO}_2\text{-O-SO}_2\text{R}^2$, e.g. $\text{CH}_3\text{-SO}_2\text{-O-SO}_2\text{-CH}_3$. In another such method, $\text{-SO}_2\text{F}$ groups are converted by reaction with $\text{R}^2\text{-SO}_3\text{H}$ and P_2O_5 .

In one embodiment of the present invention, the polymer additionally comprises second pendent groups which include groups -Ar , wherein each Ar is selected
20 independently from aromatic groups containing 6-24 carbon or nitrogen atoms and wherein each Ar may be substituted. Typical Ar groups include phenyl, naphthyl, anthracyl, phenanthracyl, biphenyl, terphenyl, fluoryl, indyl, fluoranthyl, pyridyl, puryl and the like. When substituents are present, they are typically electron donating substituents, such as alkoxy, hydroxy, amine, alkyl and the like. The second pendent
25 groups may be introduced into the polymer by ter-polymerization with monomers such as $\text{CF}_2=\text{CY-R}^{20}$ where Y is typically F but may also be CF_3 , and where R^{20} is the second pendant group. In an alternative embodiment, first pendant groups R^{20} may be added to the backbone by grafting. Second pendent groups R^{20} may be according to

the formula $-R^1-Ar$, where R^1 is as described above. In this embodiment of the invention, the polymer is crosslinked by joining first and second pendent groups. Additional crosslinking agent, described below, may be added but is unnecessary. The second pendent groups are present in the polymer in a numerical (molar) amount that is less than the amount of the first pendent groups, typically less than 90% relative to the amount of the first pendent groups and more typically less than 50%.

In one embodiment of the present invention, the polymer is crosslinked by reaction with a crosslinking agent according to the formula Ar_nR^1 , wherein Ar is as described above, wherein R^1 is a direct bond or an aromatic or aliphatic linking group, wherein R^1 may be straight-chain, branched, cyclic, heteroatomic, polymeric, halogenated, fluorinated or substituted, and where n is at least 2. n is typically 2-4, more typically 2-3, and most typically 2. R^1 typically contains 1-120 carbon, oxygen or nitrogen atoms, but may be larger if it is polymeric. R^1 is typically aliphatic. R^1 is more typically a straight-chain or branched alkylene, alkoxy or polyether group containing 1-20 carbon or oxygen atoms. R^1 may also be a polymer or oligomer, especially where n is a larger number, e.g. greater than four. R^1 is typically fluorinated, more typically highly fluorinated, and most typically perfluorinated. Where R^1 is a direct bond, n must be 2 and the crosslinking agent is Ar-Ar, e.g., biphenyl. Typically, R^1 attaches to each Ar through an oxygen atom. Typically R^1 is $-O-R^3-O-$, where R^3 is an aliphatic linking group containing 1-18 carbon or oxygen atoms, more typically containing 1-8 carbon or oxygen atoms. Examples of crosslinking agents according to the present invention include: diphenyl ether, diphenoxy alkanes, diphenoxy ethers, diphenoxy polyethers, and the like.

The crosslinking agent and polymer may be mixed by any suitable method, including mixing in solution or suspension, kneading, milling, or the like. The amount of crosslinking agent mixed with the polymer is typically selected so that the resulting crosslinked polymer will meet the hydration product and equivalent weight parameters described below.

In one embodiment of the present invention, the polymer or polymer/crosslinking agent blend is formed into a membrane prior to crosslinking. Any

suitable method of forming the membrane may be used. The polymer is typically cast from a suspension. Any suitable casting method may be used, including bar coating, spray coating, slit coating, brush coating, and the like. Alternately, the membrane may be formed from neat polymer in a melt process such as extrusion. After forming, the membrane may be annealed. Typically the membrane has a thickness of 90 microns or less, more typically 60 microns or less, and most typically 30 microns or less. A thinner membrane may provide less resistance to the passage of ions. In fuel cell use, this results in cooler operation and greater output of usable energy. Thinner membranes must be made of materials that maintain their structural integrity in use.

The crosslinking reaction may be carried out by any suitable method. Typically, the reaction is accomplished by application of heat, typically to a temperature of 160 °C [??] or more. Typically, a catalyst such as a Lewis acid is introduced. The step of crosslinking the polymer may occur in whole or part during annealing of the membrane or may be carried out separate from any annealing step. During the crosslinking step, aromatic sulfone groups are formed according to the formula: $\text{-SO}_2\text{Ar-}$. Where a crosslinking agent is used, the resulting crosslinks comprise units according to the formula $(\text{-SO}_2\text{Ar})_n\text{R}^1$. Where first and second pendent groups join to form crosslinks, they comprise units according to the formula $\text{-SO}_2\text{Ar-}$.

After crosslinking, the remaining sulfur-containing functions of the pendant groups may be converted to sulfonic acid form by any suitable process. Sulfonyl halide groups may be converted by hydrolysis. In one typical process, the polymer is immersed in an aqueous solution of a strong base and subsequently acidified. In one typical embodiment, a polymer membrane is immersed in 15% KOH in water at 80 °C for 1 hour, then washed twice in 20% nitric acid at 80 °C, then boiled in deionized water twice. Sulfonyl anhydride groups may be converted by hydrolysis, with removal of remaining $\text{R}^2\text{-SO}_3\text{H}$.

The acid-functional pendant groups typically are present in an amount sufficient to result in an hydration product (HP) of greater than 15,000, more typically greater than 18,000, more typically greater than 22,000, and most typically greater than 25,000.

In general, higher HP correlates with higher ionic conductance.

The acid-functional pendant groups typically are present in an amount sufficient to result in an equivalent weight (EW) of less than 1200, more typically less than 1100, and more typically less than 1000, and more typically less than 900.

5 In a further embodiment, the polymer or polymer/crosslinking agent blend may be imbibed into a porous supporting matrix prior to crosslinking, typically in the form of a thin membrane having a thickness of 90 microns or less, more typically 60 microns or less, and most typically 30 microns or less. Any suitable method of imbibing the polymer into the pores of the supporting matrix may be used, including overpressure, vacuum, wicking, immersion, and the like. The polymer becomes embedded in the
10 matrix upon reaction of the amidine groups. Any suitable supporting matrix may be used. Typically the supporting matrix is electrically non-conductive. Typically, the supporting matrix is composed of a fluoropolymer, which is more typically perfluorinated. Typical matrices include porous polytetrafluoroethylene (PTFE), such as biaxially stretched PTFE webs.

15 It will be understood that membranes made according to the method of the present invention may differ in chemical structure from those made by other methods, in the structure of crosslinks, the placement of crosslinks, the placement of acid-functional groups, and the like.

This invention is useful in the manufacture of polymer electrolyte membranes
20 for use in electrolytic cells such as fuel cells.

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and principles of this invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth hereinabove.

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